

The curve in Figure 16.11 of the text shows how the vibrational heat capacity depends on temperature. Note that even when the temperature is only slightly above the vibrational temperature, the heat capacity is close to its equipartition value.

The total heat capacity of a molecular substance is the sum of each contribution (Figure 16.12 of the text). When equipartition is valid (when the temperature is well above the characteristic temperature of the mode $T \gg \theta_M$) we can estimate the heat capacity by counting the numbers of modes that are active. In gases, all three translational modes are always active and contribute $\frac{3}{2}R$ to the molar heat capacity. If we denote the number of active rotational modes by ν_R^\ddagger (so for most molecules at normal temperatures $\nu_R^\ddagger = 2$ for linear molecules, and 3 for non-linear molecules), then

the total heat capacity is given by $C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$, where ν_V is the number of active vibrational modes. In the equipartition limit $\nu_V = 6$ for linear molecules and $\nu_V = 9$ for non-linear molecules. The total heat capacity is then

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$$

The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes. If the temperature is low compared to the characteristic temperatures of the modes, then the heat capacity is low. For example, for a diatomic molecule, the characteristic temperatures are $\theta_{tr} = 1.04 \text{ K}$, $\theta_{rot} = 2.07 \text{ K}$, and $\theta_{vib} = 3300 \text{ K}$. At room temperature, $T = 298 \text{ K}$, the translational and rotational modes are active, but the vibrational modes are not. The total heat capacity is then $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R = \frac{5}{2}R$. At high temperatures, $T \gg \theta_{tr}, \theta_{rot}, \theta_{vib}$, all modes are active and the total heat capacity is $C_{V,m} = \frac{3}{2}R + \frac{2}{2}R + \frac{6}{2}R = \frac{11}{2}R$. The equipartition limit is only valid when the temperature is high compared to the characteristic temperatures of the modes.

Solutions to exercises

The thermal energy is given by $E_{th} = \frac{3}{2}Nk_B T$, where N is the number of molecules. The thermal energy is then $E_{th} = \frac{3}{2}Nk_B T = \frac{3}{2} \times 6.022 \times 10^{23} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 2.71 \times 10^5 \text{ J}$.

$$E_{th} = \frac{3}{2}Nk_B T = \frac{3}{2} \times 6.022 \times 10^{23} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 2.71 \times 10^5 \text{ J}$$

At room temperature, the thermal energy is $E_{th} = 2.71 \times 10^5 \text{ J}$.

$$E_{th} = \frac{3}{2}Nk_B T = \frac{3}{2} \times 6.022 \times 10^{23} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 2.71 \times 10^5 \text{ J}$$

The thermal energy is

$$E_{th} = \frac{3}{2}Nk_B T = \frac{3}{2} \times 6.022 \times 10^{23} \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} = 2.71 \times 10^5 \text{ J}$$

$$C_{V,m} = \frac{3}{2}R + \frac{\nu_R^\ddagger}{2}R + \frac{\nu_V}{2}R$$

At room temperature $T = 298 \text{ K}$,

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